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Kinetics and Mechanism of Pd(II) Catalyzed Oxidation of Valine and Leucine by Acidic Solution of Chloramine-T

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The kinetics of oxidation of amino acid (valine and leucine) by acidic solution of chloramine-T have been studied in the presence of $PdCl_2$ as catalyst. The order of reaction in chloramine-T and substrate is unity but the acidic medium (H^+) shows inverse first order. The reaction also shows first order with respect to Pd(II) under experimental conditions. ($[H^+] >> [PdCl_2]$). A mechanism involing [Pd(II) - AA] (where AA = amino acid) intermediate complexes is proposed.

Key Words: Kinetics, Pd(II), Oxidation, Valine, Leucine, Chloramine-T.

INTRODUCTION

Kinetic studies on the catalysed oxidation of amino acids with different oxidants like pyridinium hydrobromide[1], benzyltrimethyl ammoniumchlorobromate[2], ethyl N-chlorocarbamate[3], N-bromobenzamide[4] using different catalysts like Ru(III), Os(VIII) and Ir(III). However there is no work on oxidation reactions of amino acids by chloramine-T (CAT) in acidic medium in presence of Pd(II) catalyst. Palladium(II) is known to catalyse various reactions[5]. Most studies using Pd(II) as a catalyst have employed in the form of palladium(II) chloride[6] and the nature of its active form in such reactions remains obscure. Hence, the effect of chloride in the reaction was studied in order to establish the active species of the catalyst. Pd(II) is known to catalyse reactions in acidic and alkaline medium both. We have undertaken the systematic study of title reaction with a view to find out the mechanistic aspects of the reaction.

EXPERIMENTAL

Reagent grade chemicals and doubly distilled water were used throughout. Aqueous solution of chloramine-T (E. Merck) was prepared always afresh and standardized iodometrically[7]. Solution of amino acids are prepared by dissolving appropriate quantity in double distilled water. A Pd(II) stock solution was prepared by dissolving known weight of palladium chloride (Fischer) in 0.20 mol dm^{-3} hydrochloric acid and standardized against EDTA. For some kinetic runs in the absence of chloride, the chloride ion in

the Pd(II) stock solution was precipitated with $AgNO_3$ and removed by repeated centrifugation. The resulting clear Pd(II) solution contained less than 1×10^{-6} mol dm^{-3}, Cl^- and Ag^+. Such low concentration of Cl^- and Ag^+ were found to have no significant effect on the reaction. The required chloride concentration was maintained with $KCl/NaClO_4$. The mixture was also maintain the required ionic strength of the medium.

RESULTS AND DISCUSSION

The reaction was carried out under pseudo-first order conditions were [AA] was always ten or more fold excess over [CAT] at constant temperature of 30 ± 0.1ºC. The reaction was initiated by mixing the requierd quantities of thermally equilibrated solution of [CAT] and [AA] which also contains the required quantities of Pd(II), NaOH and KCl. The progress of the reaction was followed by iodometric determination of the unreacted oxidant in aliquots (10 mL each) of the reaction mixture withdrawn at regular time intervals. The first order rate constant were obtained from the plots of -(dc/dt) *vs.* concentration of reactant. Most of the kinetic runs were followed to more than 80% completion of the reaction and rate constants were reproducible within ± 5%.

Stoichiometry and reaction products: Different reaction mixtures containing different sets of reactant concentrations at constant acidity and ionic strength were kept to react for 24 h at 30 ± 1.0ºC and then analyzed. The remaining CAT was assayed iodometrically. Under the condition [AA] > [CAT] the unreacted amino acid was estimated. The results was in agreement with 1:1 stoichiometry. Aldehydes are the main product as detected by the method reported[8].

$$\underset{\text{(Amino acid)}}{R{-}CH(NH_2)COOH} + \underset{\text{(CAT)}}{CH_3C_6H_4SO_2NClNa} + H_2O \longrightarrow CH_3C_6H_4SO_2NH_2 + RCHO + Na^+ + CO_2 + NH_3 + Cl^-$$

Reaction order: The reaction order in each reactant was obtained from (-dc/dt) *vs.* concentrations plots. The order in [CAT] was unity in the concentration range 1.0×10^{-4} to 5.0×10^{-4} mol dm^{-3} at fixed [AA], [Pd(II)], [$HClO_4$] and ionic strength (μ).

The rate constant increased linearly with increase in [AA] and the order in [AA] was found to be unity. The reaction rate increased with increase in [Pd(II)] and the order in [Pd(II)] was found to be unity. The inverse first order kinetics observed with [H^+] and there is no effect of ionic strength of medium (Table-1, Fig. 1).

Effect of added chloride: Palladium(II) is known to form different chloride complexes[9] of the general formula $Pd(Cl)_n^{(1+n)+}$ with n having values from 1 to 4. Hence the effect of chloride on the raction rate was studied. Although the stock solution of Pd(II) contained chloride, for this

TABLE-1
EFFECT OF VARIATION IN [AA], [CAT], [Pd(II)] AND [H^+] ON PALLADIUM(II) CATALYZED CAT OXIDATION OF AMINO ACIDS IN ACIDIC MEDIUM AT 30ºC

10^4[CAT] (mol dm^{-3})	10^3[AA] (mol dm^{-3})	10^5[Pd(II)] (mol dm^{-3})	10^3[H^+] (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})	
				Valine	Leucine
1.00	0.50	2.00	5.00	2.22	2.42
2.00	0.50	2.00	5.00	2.31	2.42
3.00	0.50	2.00	5.00	2.31	2.30
4.00	0.50	2.00	5.00	2.42	2.37
5.00	0.50	2.00	5.00	2.36	2.49
2.00	0.50	2.00	5.00	0.63	0.65
2.00	1.00	2.00	5.00	1.31	1.42
2.00	1.50	2.00	5.00	1.72	1.83
2.00	2.00	2.00	5.00	2.34	2.55
2.00	2.50	2.00	5.00	2.97	3.26
2.00	0.50	0.50	5.00	0.80	0.75
2.00	0.50	1.00	5.00	1.57	1.70
2.00	0.50	1.50	5.00	2.53	2.21
2.00	0.50	2.00	5.00	3.12	2.88
2.00	0.50	2.50	5.00	4.10	3.71
2.00	0.50	2.00	1.00	9.09	5.60
2.00	0.50	2.00	2.00	7.42	4.30
2.00	0.50	2.00	3.00	5.09	3.25
2.00	0.50	2.00	4.00	3.66	2.15
2.00	0.50	2.00	5.00	1.86	1.06

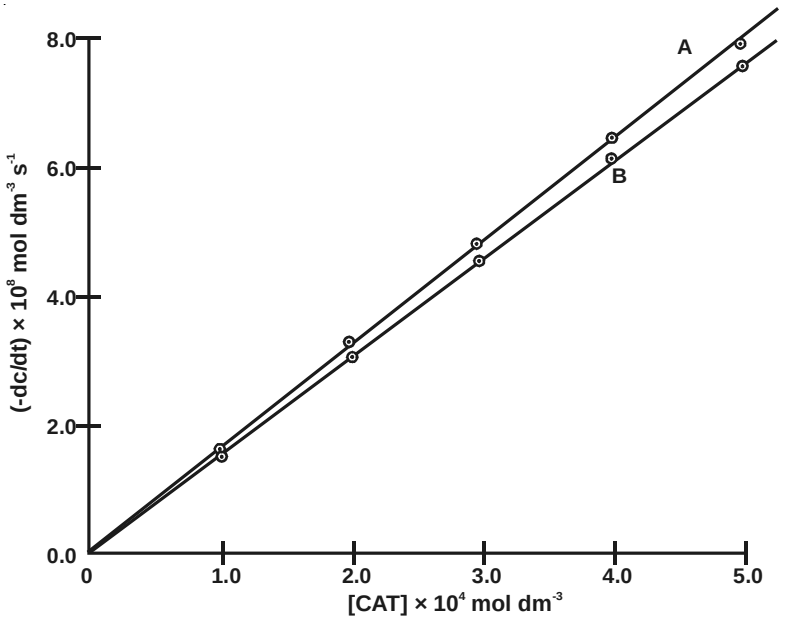

Fig. 1. In the oxidation of valine (A) and leucine (B) under the condition of Table-1

series of runs, a Pd(II) solution which did not contain chloride was used. However it was found that chloride has no effect on the reaction rate. Hence, palladium chloride complexes are precluded in the title reaction.

Effect of added *p*-toluene sulphonamide: *p*-Toluene sulphonamide (PTS) which is a reduction product of chloramine-T has no effect on the reaction, it is confirmed by the addition of P.T.S. in the reaction mixture.

Effect of temperature: Kinetics were studied at 25, 30, 35 and 40ºC with [CAT] = 2.00×10^{-4} mol dm^{-3}, [AA] = 0.50×10^{-3} mol dm^{-3}, $[H^+]$ = 5.00×10^{-3} mol dm^{-3}. The rate constants of the slow step (k) were obtained at different temperatures by graphical method. The energy of activation is calculated with the help of Arrhenius plot and other thermodynamic parameters are calculated by use of energy of activation (Table-2).

TABLE-2
THERMODYNAMIC PARAMETERS

Amino acid	Ea KJ mol^{-1}	log A	ΔS J K^{-1} mol^{-1}	ΔH KJ mol^{-1}	ΔG KJ mol^{-1}
Valine	50.23	4.79	-157.13	47.71	93.32
Leucine	55.77	5.76	-138.19	53.25	95.12

The reaction is first order each in [CAT], [Pd(II)], [AA] and shows inverse first order in $[H^+]$. The results suggests the complex formation between the catalyst and substrate. As platinum group metals have the ability to form complexes with organic substrates highly enhanced rates substantiate the formation of [Pd(II)-AA] complex; which slowly reacts with [CAT] species in the rate determining step to give products. It is also noteworthy that the reaction is not influenced by chloride ions, to be expected in Pd(II) catalysed reaction[10,11].

Taking all the experimental results into consideration a mechanism may be proposed as -

$$\underset{C_1}{[PdCl_4]^{2-}} + AA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C_2}{[PdCl_4 - AA]^{3-}} + H^+ \quad (1)$$

$$C_2 + CAT \xrightarrow{k} [PdCl_4]^{2-} + Product \quad (2)$$

Where AA represent amino acids.
Rate of loss of [CAT]

$$-\frac{d[CAT]}{dt} = k[CAT][C_2] \quad (1)$$

Applying steady state approximation for $[C_2]$

$$-\frac{d[C_2]}{dt} = k_1[C_1][AA] - k_{-1}[C_2][H^+] - k[C_2][CAT] = 0$$

$$[C_2] = \frac{k_1[C_1][AA]}{k_{-1}[H^+] + k[CAT]} \quad (2)$$

by eqn (1) and (2)

$$-\frac{d[CAT]}{dt} = \frac{kk_1[C_1][AA][CAT]}{k_{-1}[H^+] + k[CAT]} \quad (3)$$

Assuming k is very small therefore $k_{-1}[H^+] >> k[CAT]$ and $K_1 = \frac{k_1}{k_{-1}}$ (here C_1 represents Pd(III)).

$$-\frac{d[CAT]}{dt} = \frac{kK_1[CAT][AA][Pd(II)]}{[H^+]} \quad (4)$$

This rate fully explains all the observed kinetics.

Negligible effect of ionic sterngth and dielectric constant on reaction rate might be due to involvement of neutral species in the reaction. The modest energy of activation and entropy of activation support the involvement of complex transition state in the catalysed reaction. The activation energy calculated for Pd(II) catalysed reaction explains the catalytic effect.

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